CHAPTER 7

SDS-INDUCED ENHANCEMENT OF THE VISCOSITY AND VISCOELASTICITY OF AQUEOUS SOLUTIONS OF PEO

7.1 Introduction

The preceding chapters deal with surfactant/polymer combinations that have hitherto not been studied. The incentive of those investigations was to reveal the relation between headgroup structure and charge, and the propensity of micelles for interaction with polymers. This chapter, in contrast, is devoted to the most widely studied[3] surfactant/polymer combination, namely sodium dodecylsulfate (SDS) and poly(ethylene oxide) (PEO), and the investigation is focussed on the rheological aspects of this system. The system PEO/SDS certainly has its advantages. Both compounds are easily available and cheap, and PEO may be purchased in a large variety of molecular weights. Furthermore, it is the pronounced hydrophilicity of PEO, which makes interaction with micelles formed from SDS (or alkylphosphates, Chapter 5) so intriguing, since hydrophobic interaction seems to play such a crucial role in the association. The binding of polymer segments onto the hydrophobic core-water interface of the micelles favors the micellization process, but is expected to be accompanied by an unfavorable transfer of the PEO segments from the aqueous phase to the surface of the micelle. Still, PEO-bound micelles of SDS are formed at a lower cmc than for unperturbed micelles, thus the stabilization of the micelle more than compensates for this unfavorable free energy for transfer of polymer segments.

The influence of PEO on micellar properties[3,58,122], like aggregation number[64-66,254], cmc[3], counterion binding[64], and solubilizing power[4,5] has been studied in considerable detail. It is also known that above a molecular weight of 4000, PEO/SDS association is independent of molecular weight[3]. Furthermore, Nagarajan[61] and Ruckenstein[71] have both proposed quantitative models for polymer-micelle association, that describe the case of PEO/SDS

interaction. Surprisingly, the influence of SDS on the properties of the polymer has remained rather unexplored, despite the wealth of research on PEO rheology[42,43].

Several authors have reported rheological studies on the influence of SDS (among other surfactants) on the viscosity of aqueous solutions of PEO[4,57,61,257,258] or PVP[4,5,59,259]. However nearly all these studies have been performed using capillary (Ubbelohde) viscometry[4,5,57,59,259], which is best suited for the measurement of the viscosity of fluids under Newtonian flow. As a consequence little information has been obtained about the changes in viscoelasticity, which is a property of non-Newtonian fluids[167] (see also sections 3.3 and 3.4 for a brief introduction into the terminology of rheology). There are two exceptions, as far as we are aware. One is a study by Lance-Gomez[257], who used stress relaxation after cessation of steady-state flow to investigate the viscoelastic properties of PEO in aqueous solutions in the presence of salt or surfactant. He found, depending on the molecular weight fraction of the polymer, an increase or a decrease in the stress relaxation (at a shear rate of 5 s^{-1}), upon addition of an alkyl benzenesulfonate. The other exception is a study by Uhl and Prud'homme[258], who observed an increase in viscosity and viscoelasticity of a PEO solution at sufficiently high SDS concentrations, but no detailed analysis of the data was presented.

In 1957 Saito[4] reported the increase in viscosity, measured by capillary viscometry, of a PVP solution upon addition of surfactant. He proposed adsorption of mutually repelling surfactant molecules, individually bound onto the polymer chain, to explain the results. As discussed in Chapter 1, the model has been modified and, instead, micelles are considered to bind to the polymer[5]. An increase in the viscosity upon SDS addition has also been observed with the use of capillary viscometry for PEO solutions[4,57,61].

Several authors have studied the influence of SDS on the rheology of cellulose derivatives like methylcellulose[51] and ethyl(hydoxyethyl)-cellulose[77]. In these cases the changes in viscosity are more complicated due to polymer aggregation in aqueous solution.

The present chapter describes a study of the rheology of an aqueous solution of 0.25 $g.dL^{-1}$ of PEO of high molecular weight (5×10^6) at various

SDS concentrations using cone-and-plate rheometry. The polymer concentration is chosen with care to be well below the overlap concentration at which PEO coils start to 'feel' each other (see also section 7.4), and to ensure also a reasonabe concentration range for polymer-micelle interaction[68]. Our equipment allowed the measurement of not only the shear rate dependence of the viscosity but also the viscoelasticity. This is a great advantage over capillary viscometry. In addition to the known increase in viscosity upon SDS addition, we find a concomitant increase in viscoelasticity. A power-law model proved adequate to describe the shear rate dependence of the viscosity. Furthermore the viscoelasticity data revealed a partial breakdown of the polymer-micelle complexes above a critical shear stress, which was not apparent from the corresponding viscosity data.

7.2 The influence of SDS on the viscosity of a PEO solution

The effect of SDS on the apparent viscosity (see section 3.3) of the 0.25 $g.dL^{-1}$ aqueous solution of PEO (mw 5×10^6) at two fixed shear rates is depicted in Figure 7.1. The curves clearly show three distinct regions, similar to previous results obtained by using capillary viscometry[57,59,61], both at low (168.3 s^{-1}) or high (2689.4 s^{-1}) shear rate. In region I, below the critical concentration for formation of polymer-bound micelles (cmc_p 5.4 mM[67]) the viscosity changes only slightly upon addition of SDS. Besides polymer coils, only free surfactant ions are present in the solution. Above the cmc_p, in region II, the viscosity increases considerably as electrostatic repulsion between the anionic micelles bound to the polymer causes the coils to expand. This increase of the viscosity can also be observed visually when swirling the solutions gently. In region III, above 20 mM SDS the viscosity levels off and a small decrease is found upon further addition of SDS. This concentration corresponds to the saturation concentration (c_{sat}), at which the maximum number of SDS micelles is bound to the polymer. This concentration is in excellent agreement with c_{sat} determined from conductivity measurements by Witte[65,68], who found that c_{sat} is 40 mM for SDS in the presence of 0.5 $g.dL^{-1}$ of PEO. Further addition of SDS results in

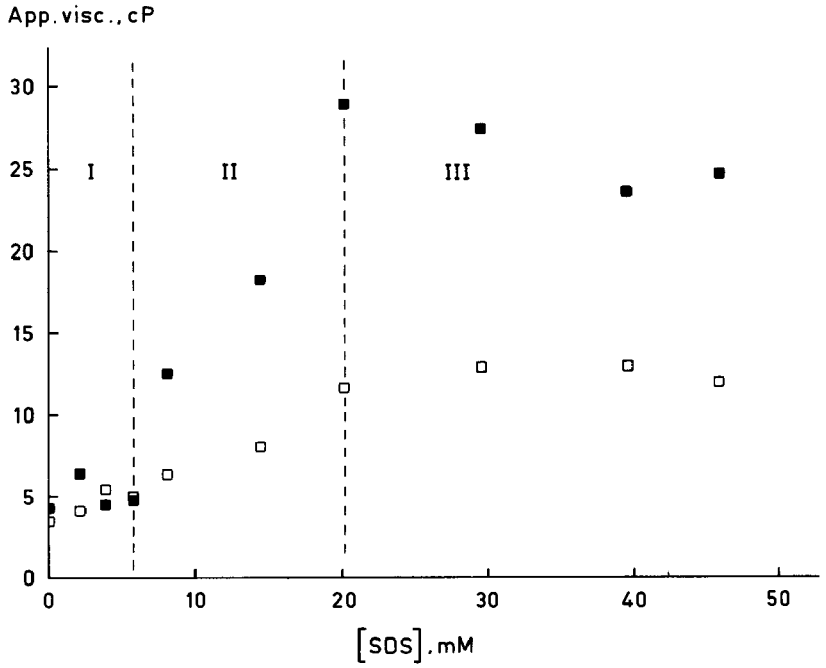

Figure 7.1 Apparent viscosity as a function of the SDS concentration at different shear rates: (■) 168.3 s^{-1}; (□) 2689.4 s^{-1}.

the formation of free micelles. The slight decrease in viscosity was explained by François et al.[57] in terms of a contraction of the extended coils, due to a decrease in electrostatic repulsion between the micelles as a result of the higher ionic strength.

The apparent viscosity of the PEO solution at a fixed SDS concentration drops with increasing shear rate, especially at SDS concentrations above the cmc_p. This is indicative of non-Newtonian behavior[167]. The data set, which consists of 11 shear rate/viscosity combinations at each SDS concentration, was analyzed according to the following simple power-law model (eq 7.1)[167], in

$$\tau = K \gamma^{n} \qquad (7.1)$$

which τ represents shear stress and γ shear rate, and in which K and n are fitting parameters. The data produce a good fit to the model (Table 7.1). It

Table 7.1 Non-Newtonian parameters K and n, and the correlation coefficient r of an aqueous PEO solution (0.25 $g.dL^{-1}$) at different SDS concentrations at 25^0C.

[SDS], mM	K, $(Pa.s)^n$	n	r
0.0	7.7	0.90	0.9982
2.2	14.7	0.84	0.9997
3.9	8.9	0.91	0.9992
5.8	5.6	0.98	0.9984
8.1	41.5	0.75	0.9983
14.4	64.4	0.74	0.9988
20.2	185.2	0.64	0.9987
29.5	97.1	0.74	0.9986
39.5	90.6	0.74	0.9982
45.9	93.1	0.74	0.9995

should be noted that K and n exhibit extremes at 6 and 20 mM of SDS, corresponding to the cmc_p and c_{sat}, respectively. The dependence of K on SDS concentration is similar to the concentration dependence of the apparent viscosity at fixed shear rate. The parameter n, which has a value of one for Newtonian liquids, decreases even further below one above the cmc_p. It is evident that binding of SDS micelles onto the PEO polymer induces increasingly non-Newtonian behavior.

7.3 The influence of SDS on the viscoelasticity of a PEO solution

An aqueous PEO solution not only exhibits viscous flow but also viscoelasticity. The latter property is of great industrial importance, since it is used to reduce 'drag' in pumping fluids through pipelines[43]. Transport of fluids is greatly facilitated if a compound is added, which

renders the liquid viscoelastic.

Viscoelasticity may be quantified as a first normal stress difference, using a cone-and-plate measuring device for the viscometer. Figure 7.2 depicts the first normal stress difference for the 0.25 $g.dL^{-1}$ PEO solution (mw 5×10^6) as a function of the shear rate for various SDS concentrations.

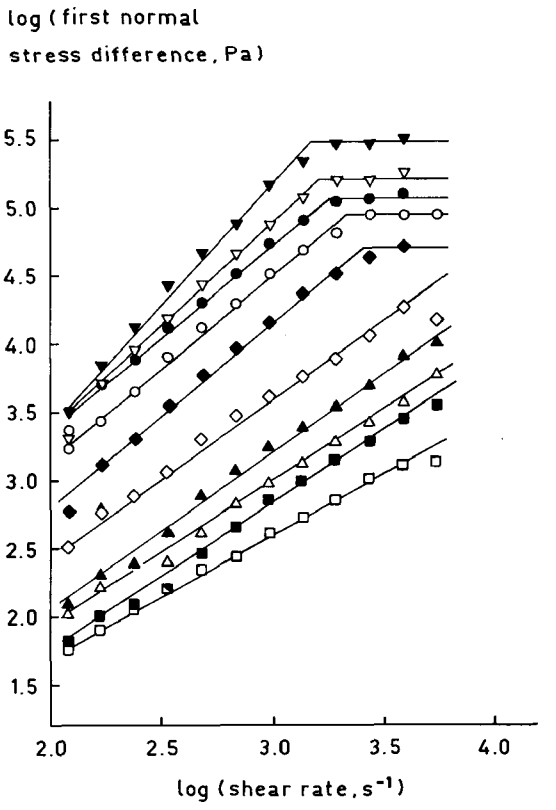

Figure 7.2 Logarithm of the first normal stress difference, indicating viscoelasticity, as a function of the logarithm of the shear rate. For clarity, each curve is shifted upward 0.2 with respect to the previous curve at lower SDS concentration. SDS concentrations: (□) 0 mM; (■) 2.2 mM; (Δ) 3.9 mM; (▲) 5.2 mM; (◇) 8.1 mM; (◆) 14.4 mM; (o) 20.2 mM; (•) 29.5 mM; (▽) 39.5 mM; (▼) 45.9 mM.

The enormous increase in first normal stress difference induced by SDS is even more obvious from Figure 7.3, which shows the first normal stress difference at fixed shear rate. The same three regions as apparent from Figure 7.1 can be distinguished. Obviously the viscoelasticity, as inferred from the first normal stress difference, is greatly enhanced when SDS micelles bind to the polymer. Another feature of Figure 7.2 is the almost constant first normal stress difference at the highest shear rates in the PEO solutions containing SDS concentrations near or above c_{sat}. From a plot of the first normal stress difference against shear stress (Figure 7.4) it is apparent that this leveling off starts at about the same shear stress of 25 Pa. This phenomenon can be interpreted as a partial breakdown of the polymer-micelle complex, mediated by

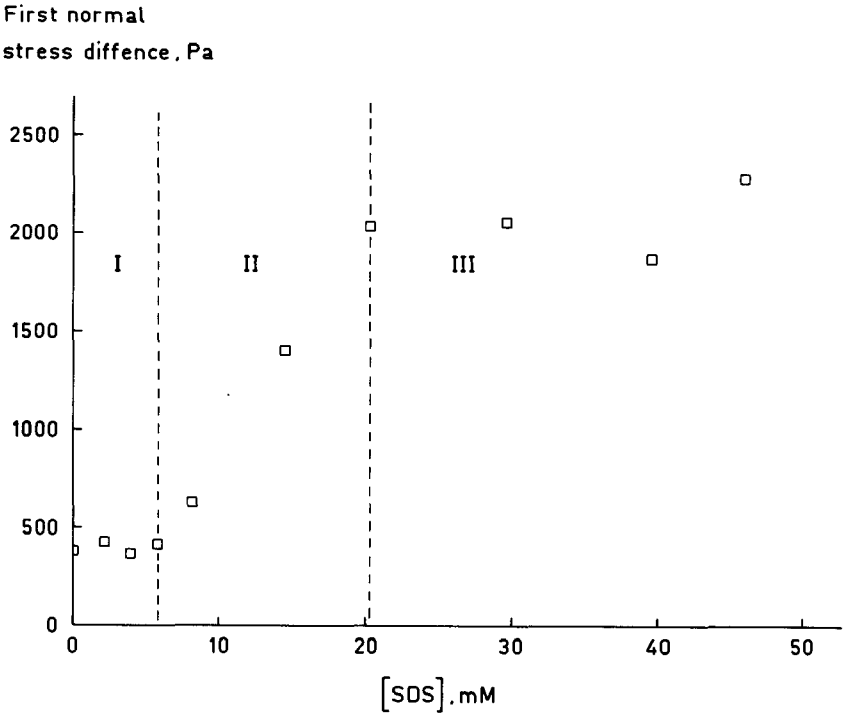

Figure 7.3 Viscoelasticity as indicated by the first normal stress difference as a function of the SDS concentration at a shear rate of 952 s^{-1}.

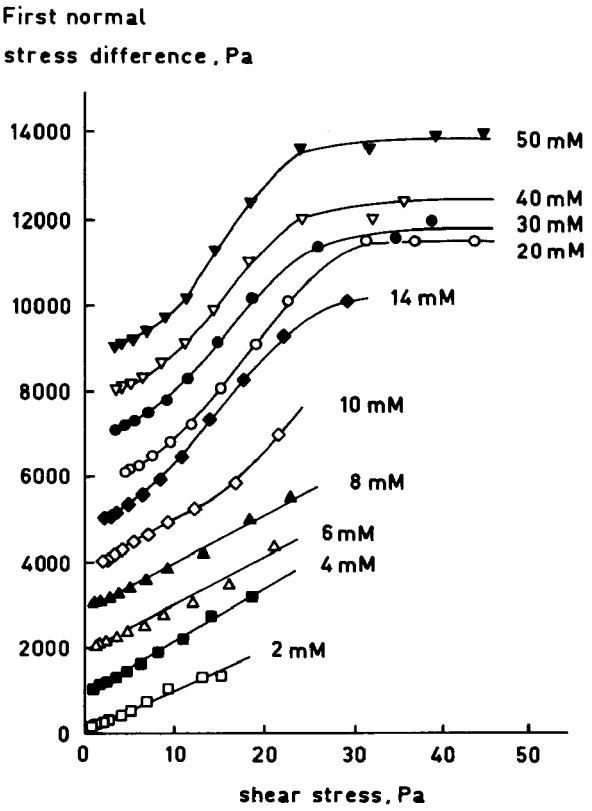

Figure 7.4 The relation between first normal stress difference and shear stress at various SDS concentrations. For clarity each curve is shifted upward 1000 Pa with respect to the previous curve at lower SDS concentration. SDS concentrations: (□) 0 mM; (■) 2.2 mM; (Δ) 3.9 mM; (▲)5.2 mM; (◇) 8.1 mM; (◆) 14.4 mM; (o) 20.2 mM; (•) 29.5 mM; (▽) 39.5 mM; (▼) 45.9 mM.

the shear stress or, more precisely, the hydrodynamic drag force[167]. If the hydrodynamic drag force exceeds the force that keeps the micelles bound to the polymer, the micelles will be ripped off. This phenomenon most likely induces the leveling off of the first normal stress differences. It must be emphasized that the binding of the micelles onto the polymer segments becomes weaker as

the SDS concentration reaches c_{sat}[165]. The reason is that the intermicellar electrostatic repulsion will increase, whereas the stabilization of the hydrophobic core-water interface remains constant. At first sight it seems surprising that the viscosity is not influenced in this region of concentration and shear rate. However, it is known that viscoelasticity is much more sensitive to shape and flexibility of polymer coils than viscosity[167].

In summary, some novel aspects of the rheology of PEO/SDS have been elucidated. The shear rate dependence of the apparent viscosity may be described by the power-law model even in the case when micelles are bound to the polymer. Furthermore, the viscoelasticity is enhanced by binding of SDS micelles, and on the basis of the data on the first normal stress difference, break-down of the polymer-micelle complex at a critical shear stress is observed. The increase in viscoelasticity may be of commercial interest, since the possibility of enhanced drag reduction is combined with the possibility to solubilize apolar compounds in aqueous solutions.

7.4 Experimental section

Materials. SDS (BDH, especially pure) and PEO (weight-averaged mw 5 x 10^6, Aldrich) were used as received. Water was deionized and distilled twice.

Rheological measurements. Solutions were prepared several hours before the measurements by adding appropriate amounts of SDS to a 0.25 $g.dL^{-1}$ aqueous solution of PEO. The overlap concentration (c^*) of PEO of this molecular weight is 0.4 $g.dL^{-1}$ and thus well above the employed concentration[52]. Furthermore, during the two weeks that are needed to ensure complete dissolution of the polymer, some degradation of PEO will be unavoidable[41a]. Therefore, the actual molecular weight will be lower and, hence, the actual overlap concentration, which is calculated as $(110 \times M^{0.5})^{-1}$, will be even higher. Rheological measurements were performed on a Brabender Rheotron rheometer with cone-and-plate geometry, equipped with a Normal F-sensor, which allows the measurement of first normal stress differences. Although some

destruction of the polymer chains was observed at higher shear rates, the corresponding effects on the viscometric data are negligible compared to the overall effects of SDS addition. Every PEO/SDS solution was only used once. All measurements were performed at 25 ^{0}C. The rheological measurements were all carried out at the Department of Chemical Technology of the University of Groningen, with the help of Dr. J.P. Sek and Prof.Dr.Ir. L.P.B.M. Janssen.